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Range in Composition and Weathering among Floating Macondo Oils during the Deepwater Horizon Oil Spill

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Abstract

Floating Macondo oils – slicks, mousses, and sheens (n=62), including "Slick A" and "Slick B" – collected from the northern Gulf of Mexico during and shortly after the *Deepwater Horizon* (DWH) oil spill were chemically analyzed to assess their range in composition/weathering. The results provide an understanding of what near-surface biota were exposed to during the spill. The following conclusions were reached:

- On average, floating Macondo oils lost 38 ± 9% of their C_5+ mass (range: 15 to 52; median: 38%) compared to fresh Macondo oil. The "freshest" floating oils, including one collected immediately upon surfacing, had already lost ~15% of the total oil mass during the oil's ascent or immediately upon surfacing.
- Although floating oils collected near (< ~5 km) the wellhead exhibited variable degrees of weathering, weathering generally increased with distance from the wellhead.
- Most mass loss was consistent with the combined effects of dissolution (both during the oil's ascent and after reaching the surface) and evaporation, within additional minor loss due to photo-oxidation (see below).
- Mass loss due to biodegradation was not evident among the oils studied; indicating biodegradation was not significant in reducing the mass of oil in coalesced slicks, mousses, and sheens during or shortly after the DWH spill.
- Trace concentrations of volatile monoaromatics (BTEX; <5.90 µg/g) were detected in floating oils indicating these compounds were not entirely dissolved during the oil's ascent.
- Severe evaporation, likely owing the high temperatures and solar radiation during the spill, depleted some n-alkanes up to about n-C_{28}. This depletion was not due to biodegradation, as evidenced by comparable depletion of n-alkanes (n-C_{17} and n-C_{18}) and isoprenoids (pristane and phytane).
- Total PAH ($TPAH_{50}$) concentrations in the floating oils averaged 6640 ± 4140 µg/g and ranged from 1,010 to 13,700 µg/g; the latter being higher than in fresh Macondo oil (13,300 µg/g) due to the concentrating effect early in weathering. On average, floating oils lost about 69 wt% of the $TPAH_{50}$ originally present in the fresh oil, with the most severely weathered floating oils losing up to 96% of the $TPAH_{50}$ originally present.
- The percent depletions of individual PAH analytes decreased with increasing ring number and degree of alkylation for homologue groups between decalins and fluoranthrenes/pyrenes. These depletions are attributable to the combined effects of evaporation and dissolution – although some depletion of individual PAH isomers and selected HPAH homologues (viz., naphthobenzothiophenes and benz(a)anthracenes/chrysenes) are consistent with photo-oxidation. Photo-oxidation is also responsible for depletion triaromatic steroid (TAS) biomarkers.

- Traces of dispersant indicators in floating oils indicates "residual" Corexit 9500 dispersant was present, which in turn, suggests "residual" dispersant may have been transported toward shore in some non-dispersed oils.
- The two floating oils collected for toxicological testing – Slick A and Slick B – were variably weathered. Slick A was less weathered than Slick B, and the former exhibits features typical of the "average" floating oils studied.

Introduction

Crude oil released (April 20 to July 15, 2010) from the Macondo well at a water depth of 1500 m following the explosion of the *Deepwater Horizon* drill rig experienced different environmental fates. Some fraction of the crude oil released remained within the deep ocean, e.g., a dissolved phase and physically or chemically-dispersed, neutrally buoyant droplets (< 40 μm) were transported laterally at depths of ~1000 to 1300 m (e.g., Camilli et al. 2010; Hazen et al 2010; Atlas 2011; Ryerson et al 2012). Buoyancy forces caused another fraction of the oil to be transported (roughly) vertically ~1500 meters through the water column to the sea surface. The oil that reached the sea surface formed multiple floating surface slicks, mousses, and sheens that were spread by wind and currents over vast areas of the northern Gulf of Mexico (GoM) during the 87-day spill (Graettinger et al 2015), before dissipating about 5 weeks after the well was capped on July 15 (Ramseur 2010).

Weathering caused by dissolution, evaporation, biodegradation and photo-oxidation affected the floating Macondo crude oil during its tenure in the environment. Vertical transport through ~1500 m of water to the sea surface provided an opportunity for dissolution of some of the more soluble chemicals present in the expelled oil prior to even reaching the sea surface. Upon reaching the sea surface evaporation, continued dissolution, photo-oxidation and perhaps even biodegradation continued to alter the floating oil during their tenure at the sea's surface and transport to shorelines. All of these weathering processes would seem to be favored in the warm surface waters (28-30°C) and high solar radiation typical of the northern GoM (Liu et al, 2014).

In addition to natural weathering processes, some fraction of the floating oil was treated with chemical dispersants in an effort to disperse the oil into the water column as a means to enhance the natural weathering processes by generating smaller droplet sizes and thereby increasing the surface area of the oil (e.g., Prince et al 2013).

The chemical composition(s) of the weathered Macondo oil from the DWH spill is an important component in assessing injury to resources in or near the sea surface, including, for example, marine mammals, turtles, sea birds, fish and fish embryos, and plankton.

A few existing studies report on the composition of a limited numbers of floating Macondo oils collected in the summer of 2010 (Aeppli et al.2012; Liu et al 2012; Aeppli et al 2014; Faksness et al 2015). These studies collectively showed the floating oils experienced changes consistent with dissolution and/or evaporation evidenced by the loss of soluble and volatile oil constituents relative to the fresh Macondo oil. In addition, marked increases in the percent mass of oxygenated hydrocarbons and decreases in some aromatic hydrocarbons (e.g., PAHs and triaromatic steroids) were attributed to photo-oxidation (Aeppli et al. 2012; 2014; Radovic et al 2014), which was also evident in laboratory studies (King et al 2014; Brakstad et al 2014). Though informative, these studies included limited numbers of samples and employed different

sample preparation and/or analytical methods than were employed in the Trustees' NRDA.

In this study, the chemical characteristics of a large population of floating Macondo oils – slicks, sheens, and mousses – collected from the sea surface before and shortly after the well was shut-in are reported. The intention of characterizing the floating oils was not to show what the character of the oil was on a specific date or at a specific location. However, the large population of floating oils studied more clearly revealed the range of composition (i.e., weathering) exhibited by floating oils, which in turn provides a basis to evaluate the range in *exposure* of near surface resources during and shortly after the DWH oil spill. These results may also prove useful in comparison to model-predicted compositions for the floating oil. A chemical fingerprinting aspect of this study also confirmed that the floating oils studied were Macondo oil, rather than naturally-occurring sheens from seeps or other oil spills in the area.

Samples and Methods

Samples

A population of 64 floating oil samples was collected from the sea surface during various offshore NRDA cruises between May 10 and July 29, 2010 (Table 1). All but two of the samples were collected before June 20 and during the active spill. The two post-June 20 samples were collected in large volume for toxicity testing on July 19 and July 29, i.e., 4 and 14 days after the well was shut-in on July 15.

The samples were collected between about 1.5 and 69 km from the Macondo wellhead (Figure 1). Most samples were collected less than 25 km and north of the wellhead in an area of the GoM that had experienced between 30 and 60 cumulative days of surface oiling (per satellite imagery; Graettinger et al 2015). No samples were collected less than 1.5 km (1 mi) from the wellhead due to restrictions on accessing this area while the spill continued.

Sample Collection

All but two of the floating oil samples were collected using pre-cleaned *Teflon* (TFE-fluorocarbon) nets obtained from General Oceanics (Miami, FL), which with the aid of a fishing pole and line or sampling wand on a telescoping pole were lowered into the surface slicks, sheens, or mousses over the sides of the ships. Before being shipped to the field for use on multiple NRDA cruises, the Teflon nets and wands were exhaustively extracted with dichloromethane (DCM) prior to being placed in clean glass jars and wrapped in pre-cleaned aluminum foil, respectively.

Per standard protocol (e.g., ASTM D4489) the floating oil samples were collected by passing the wand/net through floating oil allowing the oil to adhere to the nets, typically turning the white nets various shades of orange or brown. Upon retrieval the oiled nets were removed from the wands and placed back into the pre-cleaned glass jars for shipment to the laboratory.

In addition to the Teflon net samples, two floating oils were collected from response vessels using mechanical skimmers, *viz.*;

- Slick A: CTC02404-02 (Table 1) was collected July 29, 2010 from a barge in Port Fourchon that contained skimmed oil from various locations.

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- <u>Slick B</u>: GU2888-A0719-OE701 (Table 1) was collected on July 19, 2010 directly from the USCG vessel *Juniper* after approximately 2 hours of skimming.

All of the samples were stored on ice (<4°C) or were frozen and shipped cold to Alpha Analytical Laboratory (Alpha; Mansfield, Massachusetts) shortly after being collected. All samples were collected as part of the Trustees' NRDA effort following normal chain-of-custody procedures.

<u>Sample Preparation and Analytical Methods</u>
The net samples were spiked with recovery surrogates and serially-extracted (3x) using fresh DCM on a shaker table. The extracts were combined, dried with sodium sulfate, concentrated, and spiked with internal standards prior to analysis. The larger volume floating oils were diluted in DCM and spiked with internal standards prior to analysis. Aliquots of each extract were used to determine the gravimetric weight of the extractable oil from each sample.

The extracts were analyzed at Alpha in accordance with the DWH Analytical Quality Assurance Plan (NOAA 2014). The analyses included:

(1) *Total Extractable Material (TEM)[1] and Saturated Hydrocarbon (SHC) Quantification and Fingerprinting*: a modified EPA Method 8015B was used to determine the TEM concentration (C_9-C_{44}) and concentrations of individual *n*-alkanes (C_9-C_{40}) and $(C_{15}-C_{20})$ acyclic isoprenoids via gas chromatography-flame ionization detection (GC/FID). Concentrations of target compounds are reported in $\mu g/g_{oil}$ (ppm).

(2) *PAH, Alkylated PAH and Petroleum Biomarkers:* a modified EPA Method 8270 was used to determine the concentration of (1) approximately 80 PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics and (2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic steroids via GC/MS operated in the selected ion monitoring mode (SIM). Concentrations of target compounds are reported in $\mu g/g_{oil}$ (ppm).

The concentrations of three Corexit (dispersant) indicator compounds (2-butoxyethanol, di(propyleneglycol)-n-butyl ethers (DPnBs), and bis-(2-ethylhexyl)fumarate) were also targeted in the PAH analysis for 52 of the floating oil samples analyzed. These concentrations are reported in $\mu g/g_{oil}$ (ppm), although these concentrations are considered semi-quantitative due to reasons explained in the AQAP and Stout (2015d).

In addition, six of the floating oil samples were also analyzed via:

(3) PIANO Fingerprinting: a modified EPA Method 8260 was used for the quantification of 87 volatile organic compounds (VOCs) via purge-and-trap (full scan) gas chromatography-mass spectrometry (GC/MS). Concentrations of target compounds are reported in $\mu g/g_{oil}$ (ppm).

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[1] Per NOAA (2014), no silica gel cleanup of the sample extracts was performed and therefore, per the AQAP, the mass measured is referred to as TEM as it includes non-hydrocarbons.

DWH-AR0038653

The TEH, SHC, PIANO, PAH and biomarker concentration data reported herein are non-surrogate corrected. The analytical results for all 64 samples were also reported through NOAA Diver, although in that case, the data were reported as surrogate corrected.

Chemical Fingerprinting Methods

The specific character of each of the floating oils was determined using a tiered oil spill fingerprinting methodology (Stout, 2015a). Briefly, this methodology involved (1) the qualitative review of GC/FID chromatograms and (2) quantitative review of 29 diagnostic ratios (DRs) based upon measured concentrations of PAHs and petroleum biomarkers. The samples were each classified into one of five categories, "A" through "E", as defined in Table 2. In practice, Macondo oil was considered to be present in all 64 of the floating oil samples studied (i.e., all 64 samples were classified as A or B; Table 1).

It is notable that these same five classifications (A, B, C, D, and E) have been used throughout the Trustees' NRDA involving chemical fingerprinting as conducted by NewFields in an effort to homogenize the classification terminology for all matrices (oily matrices, sediments, and tissues) in regard to the impact/presence of Macondo oil.

Degree of Weathering Quantification

The degree of weathering in each of the floating oils comprised of Macondo oil (i.e., fingerprint classifications of A or B; Table 1) was determined based upon mass losses relative to the conservative internal marker within the oil, viz., $17\alpha(H),21\beta(H)$-hopane (referred to hereafter as "hopane"), which has proven recalcitrant to biodegradation (Prince et al. 1994) and photo-oxidation (Garrett et al. 1998). This approach was used to estimate the percent total depletion of the liquid oil (C_1-C_6 gases excluded) using the following formula:

$$\%\text{Total Oil Depletion} = [1-(H_0/H_s)] \times 100 \qquad Eq.\ (1)$$

where H_0 and H_s are the concentrations of hopane ($\mu g/g_{oil}$) in the average, fresh Macondo source oil (68.8 $\mu g/g$; Stout, 2015b) and floating oil sample, respectively. The percent depletion of any given fraction (e.g., total PAHs) or individual chemicals (e.g., naphthalene) in the floating or stranded oils was estimated using the following formula:

$$\%\text{Depletion of A} = [((A_0/H_0) - (A_s/H_s))/(A_0/H_0)] \times 100 \qquad Eq.\ (2)$$

Where A_s and H_s are the concentrations of the target analyte and hopane in the floating oil sample, respectively, and A_0 and H_0 are the concentrations of the target analyte and hopane in the average, fresh Macondo source oil (all concentrations as $\mu g/g_{oil}$). Although hopane can be degraded under some circumstances, if it (H_s) were in a given sample, any % depletions calculated would be underestimated.

As is common practice, and in order to eliminate the effects of varying surrogate recoveries on the %loss calculations, non-surrogate corrected concentrations are used in all calculations. Total oil depletion and individual mass losses calculated by these methods account only for mass loss from the liquid oil, i.e., they do not account for mass losses of gases (C_1-C_5) originally present in the Macondo oil.

Results and Discussion

<u>Floating Oil Chemical Fingerprinting</u>
Chemical fingerprinting of the 64 floating oil samples resulted in the classifications given in Table 1 (as defined in Table 2). The method used in reaching these classifications was described elsewhere (Stout, 2015a). In summary:

- Sixty-two (62) of the floating oils were consistent with Macondo oil and were given a classification of A.
- Two (2) of the floating oils were mostly consistent with Macondo oil and were given a classification of B.

None of the floating oil samples collected were inconsistent with Macondo oil, i.e., derived from another source (classification of E).

The two samples given a B classification were the result of a low concentration of oil on the net (JF2-4km-surf-0net-20100529-N310) or mixing of Macondo crude oil with a hydraulic oil (JF2-2km-surf-0net-20100530-N408). When the hydraulic oil was spilled and mixed with the crude oil is unknown.

Thus, perhaps not surprisingly given their being collected during or shortly after the active DWH oil spill, Macondo oil comprised all 64 of the floating oils shown in Figure 1. The chemical fingerprinting results, however, corroborate satellite imagery that had shown the vast aerial extent of floating oil that existed in the nearly 3 months following the blowout (Graettinger et al 2015; Fig. 1).

<u>Range of Weathering among Floating Oils</u>
Bulk chemical SARA analysis of the two large volume floating oils (Slick A and B) had shown them to be enriched in resins and asphaltenes and depleted in aromatics and (to a lesser degree) saturated hydrocarbons compared the fresh (laboratory-topped) oil (Stout 2015c). These bulk changes reflect the obvious changes in composition that the Macondo oil experienced between its release in the deep-sea and transport to and/or tenure upon the sea surface. More detailed compositional changes are revealed by the detailed chemical data collected on the floating Macondo oils studied herein. In the discussion that follows, these details are reviewed for the 62 floating oil samples given a match classification of "A". (The detailed compositions of the two "B" samples are less representative due to the issues noted above.)

The total oil depletion (*Eq.* 1) among the 62 floating oils ranged from 15% to 52% and averaged 38 ± 9.5% (median: 38%). Thus, on average, the floating oils contained only 62 ± 9.5% of the mass of original *liquid* oil released at the wellhead. (Remember this mass loss does not include C_1 to C_5 gases.)

Graphs showing the % total oil depletion versus date of collection and distance from the wellhead are shown in Figure 2. Inspection reveals there is no linear relationship between the extent of weathering of the floating Macondo oils and their collection date or distance from the well. Samples collected on or around the same date or less than about 5 km from the wellhead exhibited a wide range of weathering (Fig. 2). The variability on any given date (Fig. 2A) is not surprising since "fresh(er)" oil was continually surfacing for nearly 3 months – and the degree of weathering of oil at any time is the result of multiple factors that include "age" (i.e., duration of time spent at the

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sea surface), sea-state conditions, physical nature of the sample (e.g., sheen *versus* emulsified slick), and exposure to dispersant.   The variability in weathering observed near(er) the wellhead (< 5 km; Fig. 2A) is not surprising since "fresh(er)" oil was continually reaching the surface *and* oil that had formerly surfaced, drifted away and come back again (due to changing currents and winds) was also present in this area. With respect to distance, however, it is notable that those samples collected further away were generally more weathered (Fig. 2B) – indicating the "freshest" oils were generally found closer to the wellhead.

Notably, one of the floating oils was collected immediately (within a few minutes) of surfacing (Fig. 2). Specifically, JF3-2km-onet-20100616-surf-N143 was collected on June 16, 2010 ~ 2 km north of the wellhead where surfacing oil droplets were observed, photographed, and video-taped as they surfaced (J.R. Payne, personal communication). Results show that even this recently-surfaced sample had lost 15% of its total oil mass (Fig. 2), suggesting the mass loss had occurred during the oil's ~1.5 km ascent to the surface or within minutes of reaching the surface.   (This 15% mass loss during ascent is consistent with earlier predictions; Daling et al 2014.)   The detailed chemical composition of this "minimally-weathered" sample is discussed in greater detail later in this report (see below).

Chemical Compositions of Floating Oils
The detailed chemical analyses performed on the 62 floating Macondo oils provide an opportunity to determine what specific chemicals/ fractions were removed from or retained within the floating oils, the latter being most relevant to the exposures experienced by near surface biota during the DWH oil spill.

BTEX in the Floating Oils: Certainly some fraction of the Macondo oil was dissolved into the water column during its approximately 1.5 km and 3 to 10 hour assent to the sea surface (Ryerson et al 2012). Previous research had shown that small alkanes and monoaromatic hydrocarbons were dissolved as buoyant oil droplets travelled to the surface (Reddy et al 2012), and therefore these compounds were at least in part depleted prior to reaching the surface. Similar dissolution weathering of oil droplets rising to the water surface through only 60 m of water was observed by Payne et al. (1980) during the shallower 1979 IXTOC I blowout in the Bay of Campeche, Mexico.

However, at least some BTEX in the Macondo oil reached the sea surface – not all of these compounds were dissolved during ascent.   For example, air samples taken near the sea surface confirm at least some fraction of the BTEX reached the sea surface as oil and evaporated.[2]   The retention of some BTEX in floating oil was confirmed in the present study.   However, only six of the 62 floating oils[3] studied were specifically analyzed for BTEX and other volatile compounds.   The BTEX concentrations detected in these six samples were:

Benzene:	not detected (nd)
Toluene:	nd to 3.9 μg/g

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[2] Response Phase air dataset available through ERMA. For example, the highest detections of benzene (290 ppbv) and toluene (960 ppbv) occurred on June 7, 2010 approximately 1.19 miles southwest of the well head.
[3] JF2-2km-surf-0-20100527-N204, JF2-4km-surf-0-20100529-N305, JF2-4km-surf-0-20100529-N305, JF2-2km-surf-0-20100530-N363, GU-10-02-007-T-05, and CTC02404-02 (Slick A). These samples' PIANO results were reported through NOAA DIVER.

<table>
<tr><td>Ethylbenzene:</td><td>nd to 0.80 μg/g, and</td></tr>
<tr><td>Total Xylenes:</td><td>nd to 5.9 μg/g.</td></tr>
</table>

These concentrations are significantly lower than the fresh Macondo oil (2350 μg/g benzene, 6500 μg/g toluene, 1270 μg/g ethylbenzene, and 9010 μg/g total xylenes; Stout, 2015b), testifying to the significant loss of these highly soluble and volatile compounds due to dissolution during the oil's ascent and dissolution and evaporation after reaching the sea surface. Nonetheless, their detection confirms at least some volatile monoaromatics had reached the surface of the GoM. This, in turn, indicates that dissolution of these chemicals continued during the oil's rise throughout the entire ~1.5 km water column (from the seafloor to the surface) above the wellhead.

n-Alkanes in the Floating Oils: The range of weathering among the floating Macondo oils studied are demonstrated in Figures 3 and 4, which show the GC/FID (TEH) chromatograms and hopane-normalized histograms for the fresh Macondo oil and two floating oils that exemplify the range of total oil depletion observed among the 62 floating Macondo oils studied. The "minimally-weathered" example (JF3-2km-onet-20100616-surf-N143; Fig. 3B) best represents the character of the Macondo oil that reached the sea surface since it was collected immediately after appearing at the surface (J.R. Payne, personal communication).

Inspection reveals a progressive and increasing loss of n-alkanes and other compounds toward the left of each of the floating oils' chromatograms. This pattern is consistent with progressive evaporation of those compounds with higher vapor pressures, although some progressive dissolution of the more soluble compounds is also likely. The least weathered of the floating oils studied demonstrated a loss of nearly all compounds below n-C_8, with at least some loss of all compounds below n-C_{13} (Fig. 3B and 4). Included within this range are, of course, the BTEX compounds discussed above. Notably, although this recently-surfaced, minimally-weathered floating oil sample was not analyzed for BTEX compounds, close inspection of its GC/FID chromatogram shows that it had retained at least some toluene, ethylbenzene, and xylenes (compare Fig. 3B, inset to Fig. 3A inset). Thus, as described above, despite being significantly depleted due to dissolution during the oil's ascent, at least some BTEX compounds reached the sea surface in floating Macondo oil.

Also important is the loss of C_5 to C_{10} aliphatic hydrocarbons in the minimally-weathered floating Macondo oil (e.g., methylcyclohexane, n-alkanes et al.; compare insets to Figs. 3A and 3B). These compounds' depletion from the floating oil may be due to a combination of dissolution during the oil's ascent or to evaporation.

The most highly weathered floating oils studied demonstrated a loss of compounds evident up to n-C_{23} with virtually no compounds below n-C_{15} remaining (Fig. 3C and 4). The loss of these minimally soluble compounds is more reasonably attributed to evaporation. Percent depletion calculations for individual n-alkanes (*Eq.* 2) indeed demonstrate a complete (100%) loss of n-alkanes up through n-C_{15} (Fig. 3C, inset). Remarkably, however, some depletion of n-alkanes is revealed all the way up to about n-C_{28} (Fig. 3C, inset), which was not visually evident in the corresponding GC/FID where depletions up to n-C_{23} are evident (Fig. 3C). This demonstrates the utility of the %depletion calculation (*Eq.* 2) and the use of corresponding histograms for revealing changes due to weathering (Fig. 3C, inset). The loss of n-alkanes up to n-C_{28} was not

uncommon among the floating oils studied, as can be seen in the average hopane-normalized distribution shown in Fig. 4.

Evaporation losses extending up to n-C_{28} are rarely recognized in oil spills (Fingas, 1994; Prince et al 2002), but can occur if conditions favor evaporation (e.g., Douglas et al 2002). In this instance it is reasonable that the high air temperatures (28-30°C) and high solar radiation in the northern GoM during the DWH spill caused severe evaporation in at least some of floating oils.

Evaporation, rather than biodegradation, is clearly responsible for the depletion of the longer chain (e.g., >C_{10}) n-alkanes observed. This is evidenced by the comparable depletions of the relatively-degradable n-alkanes (n-C_{17} and n-C_{18}) and relatively-resistant isoprenoids (Pr and Ph) in the floating oils (e.g., Fig. 3C, inset); i.e., compound pairs with comparable vapor pressures. In addition, ratios of nC_{17}/Pr and nC_{18}/Ph in the floating oils samples least affected by evaporation (e.g., Fig. 3B) closely matched those of the fresh oil (~1.6 and 2.4, respectively).

The apparent lack of biodegradation of n-alkanes among the floating oils studied contrasts that observed in laboratory studies (Bacosa et al 2015). This disparity is likely explained by the low concentration of oil used in laboratory study, compared to the coalesced slicks, mousses, and sheens sampled in the present study. This is an important difference since biodegradation in coalesced floating oil must occur at the oil-water interface and in the presence of nutrients (e.g., nitrogen and phosphorous; Prince et al 2013). The apparent lack of biodegradation in the coalesced floating oils studied was likely limited due to the mass of oil not in contact with water and by the availability of nutrients in GoM surface water (Edwards et al 2011).

A comparison of the concentrations of two compounds with comparable vapor pressures but dissimilar aqueous solubilities – *viz.*, naphthalene and n-C_{12} – provides evidence that dissolution indeed affected the floating oils. Figure 5 shows a cross-plot of the concentrations of these compounds in the 62 floating oils studied. The fresh Macondo oil contained 7610 μg/g n-C_{12} and 964 μg/g naphthalene (Stout, 2015b), a nearly 8:1 proportion yielding the straight red line shown in Figure 5. Nearly all of the floating oils studied plot below the red line indicating they contain less naphthalene than would be expected if evaporation alone were responsible for the varying concentrations. This demonstrates that naphthalene was dissolved into seawater during the oil's ascent or while at the surface. Support for the former is the detection of naphthalene and other lower-molecular-weight PAH in the dissolved phase within the subsea plume (Payne and Driskel, 2015).

Polycyclic Aromatic Hydrocarbons in the Floating Oils: Table 3 contains the average, minimum, and maximum concentrations of the PAH and related compounds (e.g., decalins and sulfur-containing aromatics) measured in the population of floating Macondo oils studied. The average concentrations of total PAHs in the fresh (Stout, 2015b) and floating oils, or TPAH$_{50}$, which is defined as the sum of 50 target analytes between naphthalene and benzo(g,h,i)perylene (excluding retene and perylene) are given at the bottom of Table 3. In summary,

- The concentration of TPAH$_{50}$ in fresh Macondo oil was 13,300 μg/g.
- The concentration of TPAH$_{50}$ in floating Macondo oils averaged 6,640 ± 4140 μg/g, and ranged from 1,010 to 13,700 μg/g.

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It's notable that during the initial phases of weathering the concentration of PAH in the floating Macondo oil actually increased slightly due to the concentrating effect of evaporation of the compounds less than n-C_{15} (as was evident in Figs. 3B and 4).

Figure 6 shows the hopane-normalized histograms for PAH and related compounds in minimally-weathered, average, and severely-weathered floating oil, and versus those of fresh Macondo oil. (The minimally- and severely-weathered oils shown are the same as were depicted in Figures 3 and 4.) Also given in Figure 6 are the $TPAH_{50}$ concentrations and their percent depletions relative to hopane (per *Eq. 2*).

Inspection reveals that minimally-weathered floating Macondo oil exhibits a PAH distribution very similar to that of the fresh Macondo oil (Fig. 6A). A 12% depletion in $TPAH_{50}$ is evident and is mostly expressed by the loss of naphthalene and methyl-naphthalenes from the floating oil (N0-N1; Fig. 6A) due to both evaporation and dissolution (Fig. 5). Despite the 12% depletion in $TPAH_{50}$, as noted above, the absolute concentration of the TPAH actually increased above that present in the fresh Macondo oil. This is possible because hopane was also concentrated during weathering.

On average, the 62 floating Macondo oils studied contained 6640 µg/g $TPAH_{50}$ (Table 3). This concentration corresponds to a 69% depletion of PAHs relative to hopane (*Eq. 2*) that is caused predominantly by the additional losses of naphthalenes and the alkyl-naphthalenes (N0-N4; Fig. 6B) along with lesser losses of the C1-C3 homologues of fluorenes, phenanthrenes/anthracenes, dibenzothiophenes and fluoranthenes/ pyrenes.

The severely-weathered floating oil contains only 1090 µg/g $TPAH_{50}$, which represents a 96% depletion compared to the fresh oil (*Eq. 2*). Lower molecular weight PAHs (LPAHs) such as naphthalenes and fluorenes are nearly completely removed (Fig. 6C) causing phenanthrenes, although depleted themselves, to become the dominant PAHs present in this sample. Most higher molecular weight PAHs (HPAHs) are also depleted and most homologous profiles show a shift toward PAHs with higher degrees of alkylation. For example, C4-fluoranthrenes/pyrenes (FP4) have become the dominant homologue among the FP series (Fig. 6C). However, a different profile is evident within the naphthobenzothiophene (NBT0-NBT4) and benzo(a)anthracene/chrysene homologues (C0 to BC4) in which the methyl-homologues (NBT-1 and BC1) have become dominant (Fig. 6C inset).

These atypical homologue patterns are likely due to the effects of photo-oxidation. Specifically, while biodegradation is considered to progress slower with increased degree of alkylation (Elmendorf et al 1994), photo-oxidation is considered to progress faster with molecular size and degree of alkylation (Prince et al 2003; Maki et al 2001,Garrett et al 1998). Thus, the skewing of the naphthobenzothiophenes and benzo(a)anthracene/chrysene homologues toward the left in the severely weathered floating oil (Fig. 6C inset) are consistent with changes caused by photo-oxidation. This is discussed further below.

The effects of weathering on individual PAH analytes and analyte groups can be seen in Figure 7, which shows the average percent depletions for individual PAHs in minimally-weathered, average, and severely-weathered floating oil, versus those of fresh Macondo oil. (The minimally- and severely-weathered oils shown are the same as were depicted in Figures 3, 4, and 6.) These graphs show the progression in weathering of the floating

oils with the minimally-weathered oil exhibiting greater depletion among the less alkylated LPAHs, dominated by losses of decalins, benzothiophenes, and naphthalenes (Fig. 7A).

As weathering of the floating Macondo oils progressed, however, it is clear that all of the LPAH and HPAH groups are affected (Fig. 7B-C). On average, the floating Macondo oils exhibit a predictable pattern of PAH weathering in which the percent depletions within most homologue groups decreases with increasing degree of alkylation (see downward pointing arrows in Fig. 7B-C). This is clearly evident in all of the homologue groups between decalins (D0-D4) and fluoranthrenes/pyrenes (FL0-FP4). In addition, these depletions tend to decrease with increasing ring number so that, for example, the depletion among naphthalenes exceeds those of fluoranthrenes/ pyrenes with losses among phenanthrenes/ anthracenes and dibenzothiophenes being mostly equal. As the floating oils became severely weathered the depletion of all LPAH and fluoranthrenes/ pyrenes increased becoming nearly complete (81 to 100%; Fig. 7C).

These patterns of losses are attributable to the combined effects of evaporation and dissolution, which would promote the loss of compounds with higher vapor pressures and aqueous solubilities. Although some impact of biodegradation of the PAHs cannot be ruled out it seems unlikely to have been significant considering that the more susceptible n-alkanes did not appear to have been depleted/biodegraded (relative to isoprenoids) in even severely-weathered floating oil (Fig. 3C). The fact that PAH depletions extend beyond the carbon range that might be expected is, perhaps not surprising given that n-alkanes up to $n-C_{28}$ are also depleted (Fig. 3C inset). As with the n-alkanes, the depletion of these seemingly non-volatile and insoluble PAH is attributed to the high air temperatures (25-30°C) and high solar radiation that existed much of the time during the active spill.

As noted above (Fig. 6C inset), it is obvious that the degree and pattern of depletion for the naphthobenzothiophenes (NBT0-NBT4) and benz(a)anthracenes/chrysenes (C0-BC4) are distinct from the other PAH homologues (Fig. 7B-C). With increased weathering of the floating Macondo oils these two homologue groups exhibited greater depletions with *increasing* degree of alkylation (see upward pointing arrows in Fig. 7B-C). This same trend has been produced in lab experiments on photo-oxidation (Garrett et al 1998; Prince et al. 2003), which indicates that the floating Macondo oils suffered some PAHs losses due to exposure to (uv) radiation.

Further evidence in support of photo-oxidation of some PAHs are the different effects evident among individual PAH isomers. For example, it is notable that benz(a)anthracene exhibited a greater depletion than chrysene at each stage of weathering (Fig. 7). This likely results from the former's *peri*-condensed structure (*versus* the latter's *cata*-condensed structure),[4] which is considered more susceptible to uv radiation due to its larger cross-sectional area (Plata et al 2008). In addition, inspection of individual methyl-fluoranthene/pyrene and methyl-chrysene isomer patterns reveals isomer-specific changes also attributable to photo-oxidation of isomers previously recognized as being relatively susceptible to photo-oxidation (Fig. 8).

The effects of photo-oxidation on Macondo oil has also been recognized by other researchers (Aeppli et al 2012; Radovic et al 2014). Establishing that photo-oxidation

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[4] peri-condensed refers to PAHs in which 3 or more rings share a common carbon atom; cata-condensed refers to PAHs in which no more than 2 rings share a common carbon atom.

has affected the floating Macondo oils is important because the process has been associated with increased toxicity of seawater in contact with photo-oxidized oils (e.g. Payne and Phillips, 1985; Lee 2003; King et al. 2014).

Biomarkers in the Floating Oils: The stability of biomarkers during weathering of spilled oil is a fundamental basis for their use in chemical fingerprinting (Wang et al 2006). The floating Macondo oils exhibited mostly stable triterpane and sterane biomarker distributions regardless of the degree of weathering, which allowed for the development and use of numerous biomarker-based diagnostic ratios (DRs) to be used in "fingerprinting" these oils (Stout, 2015a).

The floating oils from the spring and summer 2010, however, exhibited marked reduction in the relative and absolute concentration of triaromatic steroid (TAS) biomarkers. This reduction can be visualized in Figure 9A, which shows the relative (hopane-normalized) abundances of triterpanes, steranes, and TAS in fresh and severely weathered floating Macondo oil.

The distributions and abundances of the individual triterpanes (T4 to T35) and steranes (S4 to S27) in the severely weathered oil closely match those in the fresh oil (Fig 9A). This indicates that, despite an increase in absolute concentrations of these biomarkers due to loss of the more volatile/soluble fraction of the floating oil, their proportions (and any associated DRs) remained mostly stable even after severe weathering of the floating oil. However, there are marked decreases in the relative abundances of the four TAS congeners measured (see white bars at the far right of Fig. 9A). These four TAS congeners exhibit percent depletions that narrowly range from 58 to 62% relative to hopane (*Eq.* 2), which indicates the process(es) responsible for their depletion has affected all four congeners similarly. This can be seen upon inspection of the corresponding extracted ion profiles for the fresh and severely weathered Macondo oils (Fig 9B and 9C, respectively).

The non-preferential depletion in the various TAS congeners was also observed by other researchers, who attributed their reduction in spilled and laboratory irradiated oils exclusively to photo-oxidation (Aeppli et al 2014; Radovic et al 2014). The photo-reactivity of the TAS congeners is not surprising given their highly alkylated PAH structures (Fig. 9A inset), which are known to be particularly photo-sensitive (Garrett et al 1998; Prince et al. 2003). The reduction of TAS is an additional line of evidence that photo-oxidation had affected the floating Macondo oil in spring and summer of 2010, which as noted above, is important given the increased toxicity of seawater associated with photo-oxidized oils (Payne and Phillips, 1985; Lee 2003, King et al. 2014).

Dispersant Indicators in the Floating Oils: BP (2014) reports about 1,073,025 gallons of dispersants were applied to *surface* waters of the Gulf of Mexico between April 22 and July 19, 2010. Both Corexit 9500 (~80% or 858,356 gallons) and Corexit 9527 (~20% or 214,669 gallons) were applied mostly (~91%) by aerial spraying with the balance from source control vessels. Thus, it is reasonable that at least some of the floating oils samples studied herein (that were collected between May 10 and June 20, 2010) may have been exposed to dispersant(s).

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Ten of the 52 floating Macondo oils analyzed for dispersant indicators[5] contained detectable concentrations, but only in three of these was the concentration of any of the dispersant indicator compounds above the reporting limit that were not "blank qualified" (Table 4). Each of these oils only contained the DPnBs, i.e., indicators for Corexit 9500. The scarcity of floating oils containing detectable dispersant indicators is not unreasonable given the function of the dispersants (i.e., to disperse floating oil). Nonetheless, detectable concentrations of DPnBs in some of the floating oils indicates not all floating oil exposed to dispersants were completely dispersed, but remained sufficiently coalesced to be sampled as a floating oil yet retain some "residual" dispersant. This observation may be important since it suggests that at least some "residual" dispersant may have been transported toward shore in coalesced oil slicks.

Large Volume Floating Oils for Toxicity Testing
As noted above, two of the 62 floating Macondo oils were collected in large volume with the intention of using these oils in toxicological testing. These oils are generally referred to as "Slick A" and "Slick B" (Table 1). The concentrations of PAHs and hopane in these oils are provided for convenience in Table 3.

Figure 10 shows a cross-plot of the %total oil and %TPAH$_{50}$ depletions for all of 62 the floating Macondo oils studied from the spring and summer of 2010. The large volume oils – Slick A and Slick B – are shown to be among the more weathered of the floating oils studied, with Slick A being somewhat less weathered than Slick B. Slick A and Slick B exhibit %total oil depletions of 40% and 48%, respectively and %TPAH$_{50}$ depletions of 68% and 85%, respectively. Slick A is, however, weathered to approximately the same degree as the average of all 62 floating oils studied (38% total oil and 69% TPAH$_{50}$). Therefore, the Slick A oil can be considered representative of the average composition of the floating oils.

Although also evident in Figure 2, it is worth reiterating that the least weathered floating oils studied, including the floating oil collected immediately upon appearing at the surface (JF3-2km-onet-20100616-surf-N143; 1007189-14D), exhibit total oil depletions on the order of 15% (Fig. 10). This suggests that 15% of the mass of the C$_5$+ oil was removed from the oil during its ascent from the wellhead (i.e., dissolution in the water column) or immediately upon reaching the surface (i.e., evaporation dominant).

Figure 11 shows the PAH and biomarker (hopane-normalized) distributions for the large volume floating oils. The effects of weathering on the PAHs in both oils are clear, and exhibit the decreased abundances of LPAH described above. The PAHs in Slick B are clearly more depleted/weathered than those in Slick A. The homologue patterns for the naphthobenzothiophenes (NBT0-4) and benz(a)anthracenes/chrysenes (BaA-BC4) show that the Slick B oil has experienced a higher degree of photo-oxidation than the Slick A oil, as evidenced by the former's greater abundance of homologues with less alkyl side-chains (Fig. 11A-11B insets). A greater degree of photo-oxidation in the Slick B oil is also evident in its lower relative abundance of TAS compounds (Fig. 11C-11D).

Finally, the two large volume floating oils were not analyzed for the dispersant (Corexit) indicator compounds; therefore it is unknown whether either contained these compounds.

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[5] dispersant indicators [2-butoxyethanol, di(propyleneglycol)-n-butyl ethers (DPnBs), and bis-(2-ethylhexyl)fumarate] were not targeted during the analysis of 10 of the floating oil samples.

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Table 1: Inventory of 64 floating oil samples collected and their fingerprinting classifications.   Fingerprint classifications refer to Table 2.

Client ID	Date Collected	Fingerprint Classification	Client ID	Date Collected	Fingerprint Classification
JF-ref-surf-0-20100510-001N	5/10/2010	A	JF2-2km-surf-0-20100530-N363	5/30/2010	A
JF-4km-surf-0-20100512-N084	5/12/2010	A	GU-10-02-005-T-02	5/30/2010	A
751001-038	5/15/2010	A	GU-10-02-004-T-01	5/30/2010	A
B30A-SP02	5/19/2010	A	GU-10-02-005-T-01	5/30/2010	A
B31A-SP04	5/19/2010	A	GU-10-02-005-T-03	5/30/2010	A
JF2-15km-surf-0-20100523-N049	5/23/2010	A	GU-10-02-005-T-001	5/30/2010	A
JF2-8km-surf-0-20100523-N058	5/23/2010	A	GU-10-02-005-T-002	5/30/2010	A
JF2-4km-surf-0-20100524-N100	5/24/2010	A	JF2-2km-surf-0net-20100530-N408	5/30/2010	B
JF2-2km-surf-0-20100524-N129	5/24/2010	A	JF2-2.5km-surf-0-20100531-N425	5/31/2010	A
JF2-4km-surf-onet-20100524-N111	5/24/2010	A	GU-10-02-006-T-01	5/31/2010	A
JF2-4km-surf-onet-20100524-N112	5/24/2010	A	GU-10-02-006-T-02	5/31/2010	A
JF2-2km-onet-surf-20100524-N139	5/24/2010	A	GU-10-02-006-T-03	5/31/2010	A
JF2-2km-surf-0net-20100524-N140	5/24/2010	A	GU-10-02-006-T-04	5/31/2010	A
JF2-2km-surf-0-20100525-N155	5/25/2010	A	GU-10-02-006-T-05	5/31/2010	A
JF2-2km-surf-onet-20100525-N156	5/25/2010	A	GU-10-02-007-T-05	6/1/2010	A
JF2-2km-surf-0net-20100525-N157	5/25/2010	A	GU-10-02-007-T-06	6/1/2010	A
JF2-2km-rov-0net-20100525-N158	5/25/2010	A	GU-10-02-007-T-01	6/1/2010	A
JF2-2km-surf-0-20100527-N204	5/27/2010	A	GU-10-02-007-T-02	6/1/2010	A
JF2-2km-surf-0net-20100527-N185	5/27/2010	A	GU-10-02-007-T-03	6/1/2010	A
JF2-2km-surf-0net-20100527-N186	5/27/2010	A	GU-10-02-007-T-04	6/1/2010	A
JF2-2km-surf-0net-20100527-N186	5/27/2010	A	GU-10-02-008-T-01	6/2/2010	A
JF2-2km-surf-0net-20100527-N187	5/27/2010	A	TJ1000SP01	6/5/2010	A
JF2-3km-surf-0-20100528-N247	5/28/2010	A	TJ1100SP01	6/6/2010	A
JF2-3km-surf-0net-20100528-N277	5/28/2010	A	JF3-2km-onet-20100616-surf-N143	6/16/2010	A
JF2-3km-surf-0net-20100528-N278	5/28/2010	A	JF3-2km-onet-20100616-surf-N143	6/16/2010	A
GU-10-02-002-T-01	5/28/2010	A	JF3-2km-0-20100616-surf-N144	6/16/2010	A
JF2-4km-surf-0-20100529-N305	5/29/2010	A	JF3-2km-onet-20100616-surf-N173	6/16/2010	A
JF2-4km-surf-0-20100529-N305	5/29/2010	A	JF3-2km-0net-20100616-surf-N142	6/16/2010	A
JF2-4km-surf-0net-20100529-N309	5/29/2010	A	JF3-2nmi-0-20100620-surf-N287	6/20/2010	A
JF2-4km-surf-0net-20100529-N312	5/29/2010	A	JF3-2nmi-onet-20100620-surf-N286	6/20/2010	A
JF2-4km-surf-0net-20100529-N310	5/29/2010	B	GU2888-A0719-OE701*	7/19/2010	A
GU-10-02-005-T-003	5/30/2010	A	CTC02404-02**	7/29/2010	A
			*Slick B		
			**Slick A		

Table 2: Chemical fingerprinting classification of floating oil samples. DRs refers to diagnostic ratios used in fingerprinting oily matrices (Stout, 2015a).

Sample's Fingerprint Classification	Description	Practical Conclusion to NRDA
A	Chromatographic features and DRs are consistent with Macondo oil or differences can unequivocally be explained by external factors*	Macondo crude oil is present
B	Chromatographic features and DRs preclude unequivocal match but differences can be reasonably explained by external factors*	
C	Not applied to oily matrices; used in the classification of sediments and tissues. Chromatographic features and DRs are equivocal but other lines of evidence support the possible presence of Macondo oil; Concentrations often low	Macondo crude oil is possibly present
D	Chromatographic features and DR are inconclusive and no other classification is justified. Most often due to a very hydrocarbon concentrations	No petroleum is obviously present
E	Chromatographic features and DRs are inconsistent with Macondo oil and cannot be explained by external factors*	Macondo oil is absent; a different petroleum is present

*For example, weathering, mixing, low(er) concentrations, and/or interferences

Table 3: Concentrations ($\mu g/g_{oil}$) of PAH analytes and hopane in fresh and floating Macondo crude oils, including the two large volume floating oils collected for toxicological testing. Concentrations are non-surrogate corrected. Fresh oil concentrations from Stout (2015b). Min and max refer to minimum and maximum concentrations of each analyte among all 62 floating oils; not any individual sample.

| Abbrev	Analytes	Fresh Macondo Oil (Avg; n=6)	Floating Macondo Oils (n=62)				Large Volume Floating Macondo Oils	
			Avg	StDev	Min	Max	Slick A	Slick B
D0	cis/trans-Decalin	779	38	85	nd	464	0.8	nd
D1	C1-Decalins	1174	89	175	nd	890	1.6	nd
D2	C2-Decalins	966	117	196	nd	949	2.7	nd
D3	C3-Decalins	436	82	115	nd	459	5.7	nd
D4	C4-Decalins	431	125	137	nd	482	69	nd
BT0	Benzothiophene	7	0.8	1.5	nd	7	nd	nd
BT1	C1-Benzo(b)thiophenes	33	6.6	7	nd	31	nd	nd
BT2	C2-Benzo(b)thiophenes	31	9.0	9	nd	32	5.9	nd
BT3	C3-Benzo(b)thiophenes	48	20	18	nd	51	19	nd
BT4	C4-Benzo(b)thiophenes	37	20	16	nd	44	24	nd
N0	Naphthalene	964	31	80	nd	389	0.2	0.3
N1	C1-Naphthalenes	2106	234	416	nd	1730	10	1.0
N2	C2-Naphthalenes	2259	587	730	1	2371	290	11
N3	C3-Naphthalenes	1597	609	597	3	1646	652	55
N4	C4-Naphthalenes	721	363	303	7	813	459	78
B	Biphenyl	204	41	56	nd	208	13	0.8
DF	Dibenzofuran	30	11	12	nd	35	8.8	0.5
AY	Acenaphthylene	9	3.0	3	nd	10	1.6	0.1
AE	Acenaphthene	21	8.1	9	nd	31	7.0	0.3
F0	Fluorene	150	60	62	nd	180	62	5.8
F1	C1-Fluorenes	308	185	158	5	444	238	55
F2	C2-Fluorenes	404	293	201	17	584	374	157
F3	C3-Fluorenes	286	247	135	28	451	290	187
A0	Anthracene	2	3.9	6	nd	20	10	3.0
P0	Phenanthrene	310	201	159	14	496	272	95
PA1	C1-Phenanthrenes/Anthracenes	676	569	317	67	1079	744	445
PA2	C2-Phenanthrenes/Anthracenes	657	650	268	143	1097	750	600
PA3	C3-Phenanthrenes/Anthracenes	381	355	142	73	575	392	326
PA4	C4-Phenanthrenes/Anthracenes	148	150	62	29	252	177	133
RET	Retene	0	nd	nd	nd	nd	nd	nd
DBT0	Dibenzothiophene	53	33	28	2	80	44	12
DBT1	C1-Dibenzothiophenes	153	128	79	16	262	166	71
DBT2	C2-Dibenzothiophenes	197	199	85	43	336	238	180
DBT3	C3-Dibenzothiophenes	146	162	57	45	263	197	172
DBT4	C4-Dibenzothiophenes	72	80.2	28	21.6	142	90.6	82
BF	Benzo(b)fluorene	11	7.5	7.6	nd	18.9	9.5	nd
FL0	Fluoranthene	4	4	2	0.6	8.4	3	3
PY0	Pyrene	16	15	8	2	28.3	16	12
FP1	C1-Fluoranthenes/Pyrenes	80	76	42	9	148	82	54
FP2	C2-Fluoranthenes/Pyrenes	130	124	72	12	239	129	74
FP3	C3-Fluoranthenes/Pyrenes	158	154	82	22	311	167	112
FP4	C4-Fluoranthenes/Pyrenes	125	139	65	32.8	299	147	119
NBT0	Naphthobenzothiophenes	18	27	6	11	41	27	26
NBT1	C1-Naphthobenzothiophenes	56	79	19	32	120	76	82
NBT2	C2-Naphthobenzothiophenes	80	100	31	32	162	107	101
NBT3	C3-Naphthobenzothiophenes	58	70	30	16	131	68	63
NBT4	C4-Naphthobenzothiophenes	37	48.0	23	11.1	100	52.8	44.9
BA0	Benz[a]anthracene	7	5	4	nd	11	6	1
C0	Chrysene/Triphenylene	56	68	13	33	92	85	85
BC1	C1-Chrysenes	129	139	40	48	219	167	152
BC2	C2-Chrysenes	158	153	67	34	290	185	142
BC3	C3-Chrysenes	156	129	75	2	288.0	158	95
BC4	C4-Chrysenes	90	77	50	0.8	196	86.3	53.1
BBF	Benzo[b]fluoranthene	6.1	7.4	1.4	3.4	10	9.0	9.0
BJKF	Benzo[jk]fluoranthene	0.5	0	0	nd	1	1	1
BAF	Benzo[a]fluoranthene	0.0	nd	nd	nd	nd	nd	nd
BEP	Benzo[e]pyrene	12	14.1	4.4	4.3	22	16.5	14.9
BAP	Benzo[a]pyrene	3.2	2.4	2	nd	6	2.5	1
PER	Perylene	1.0	0.8	0.8	nd	3	0.2	nd
IND	Indeno[1,2,3-cd]pyrene	1.2	0.6	0.8	nd	4	0.9	0.6
DA	Dibenz[a,h]anthracene	2.5	1.9	1.3	nd	5.1	2.3	1.0
GHI	Benzo[g,h,i]perylene	2.3	2	1	1	5	3	2
	Hopane	68.8	112	16	80	144	115	132
	TPAH50 (N0-GHI, excl. RET & PER)	13300	6640	4140	1010	13700	7090	3920

Table 4: Inventory of floating oils containing detectable dispersant indicators.
42 other oils contained no detectable dispersant indicators, including the Slick A and Slick B samples.   Absolute concentrations (μg/g$_{oil}$) are estimated and not surrogate-corrected.   J-value below reporting limit, B-detected concentration < 3-times that detected in the laboratory blank.

	2-butyoxy-ethanol		Glycol Ether Isomers (DPnBs)		Bis-(2-ethyl-hexyl) fumarate
JF2-2km-surf-0net-20100527-N187	0.6	J	16		nd
GU-10-02-002-T-01	nd		9		nd
GU-10-02-004-T-01	nd		8		nd
JF2-2km-surf-0net-20100525-N157	nd		3	J	nd
JF2-3km-surf-0net-20100528-N277	nd		3	B	nd
JF2-2km-surf-0net-20100527-N185	nd		2	B	nd
JF2-2km-surf-0net-20100524-N140	nd		2	J	nd
JF2-4km-surf-0net-20100529-N309	nd		2	JB	nd
JF2-2km-rov-0net-20100525-N158	nd		2	J	nd
JF2-4km-surf-0net-20100529-N312	nd		1	J	nd
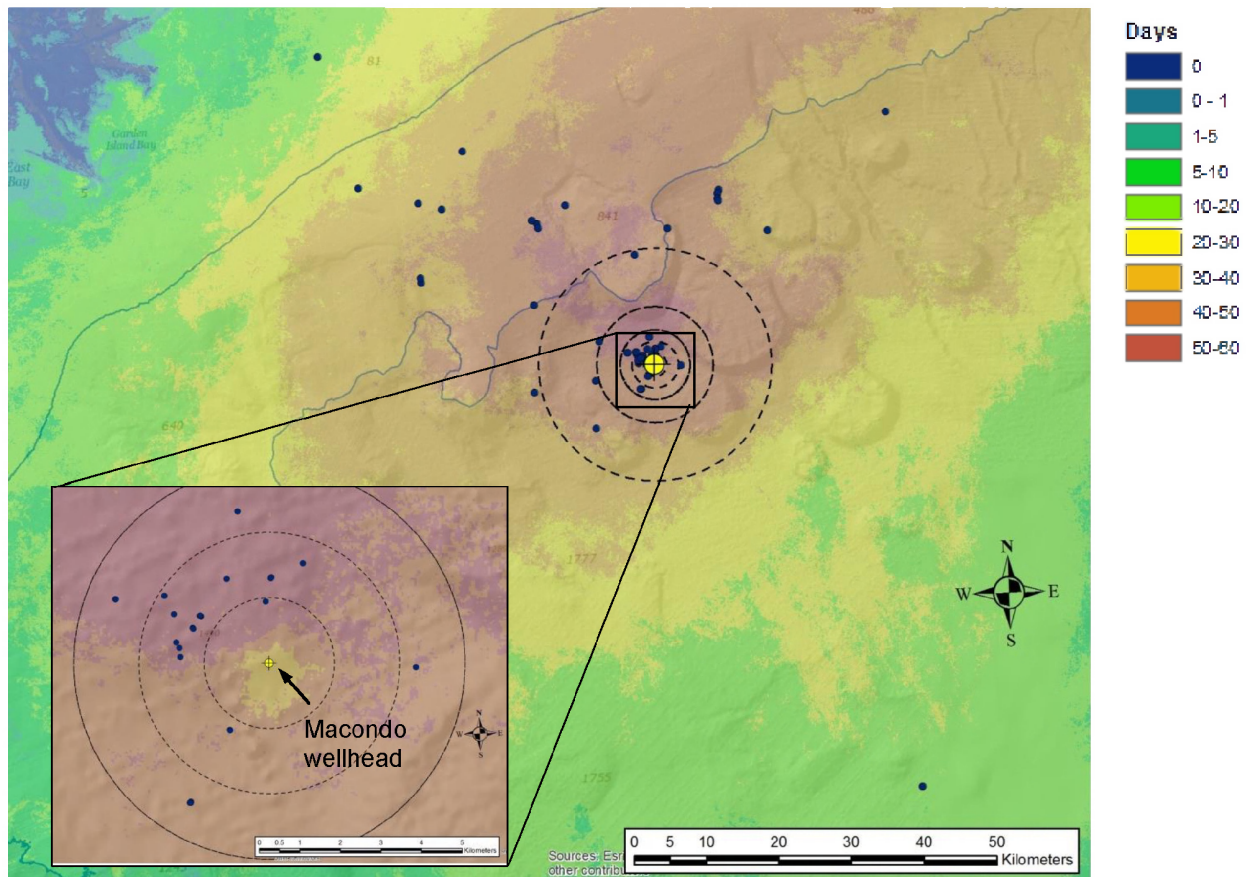
Figure 1: Map showing the location of 64 floating oil samples studied relative to cumulative surface oil days (after Graettinger et al 2015). Concentric circles show distance from the well head (1, 3, 5 and 10 miles).
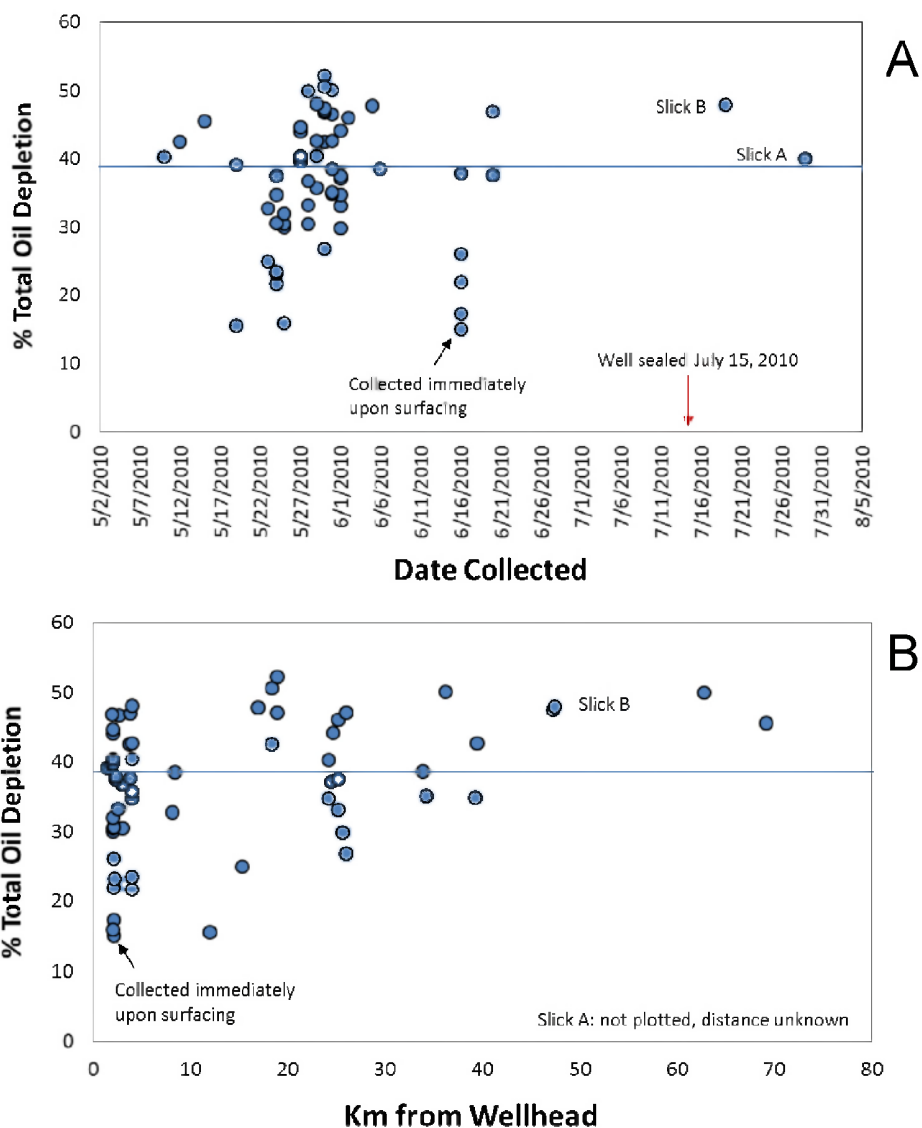
Figure 2: Plots of the weight percent total oil depletion (weathering) in floating Macondo oils versus (A) the date of collection and (B) distance from the Macondo well (km). Horizontal line depicts average depletion (38 ± 9.5). Median depletion was also 38%. Note the "freshest" samples, even when collected immediately after surfacing, had lost about 15 wt% of mass.
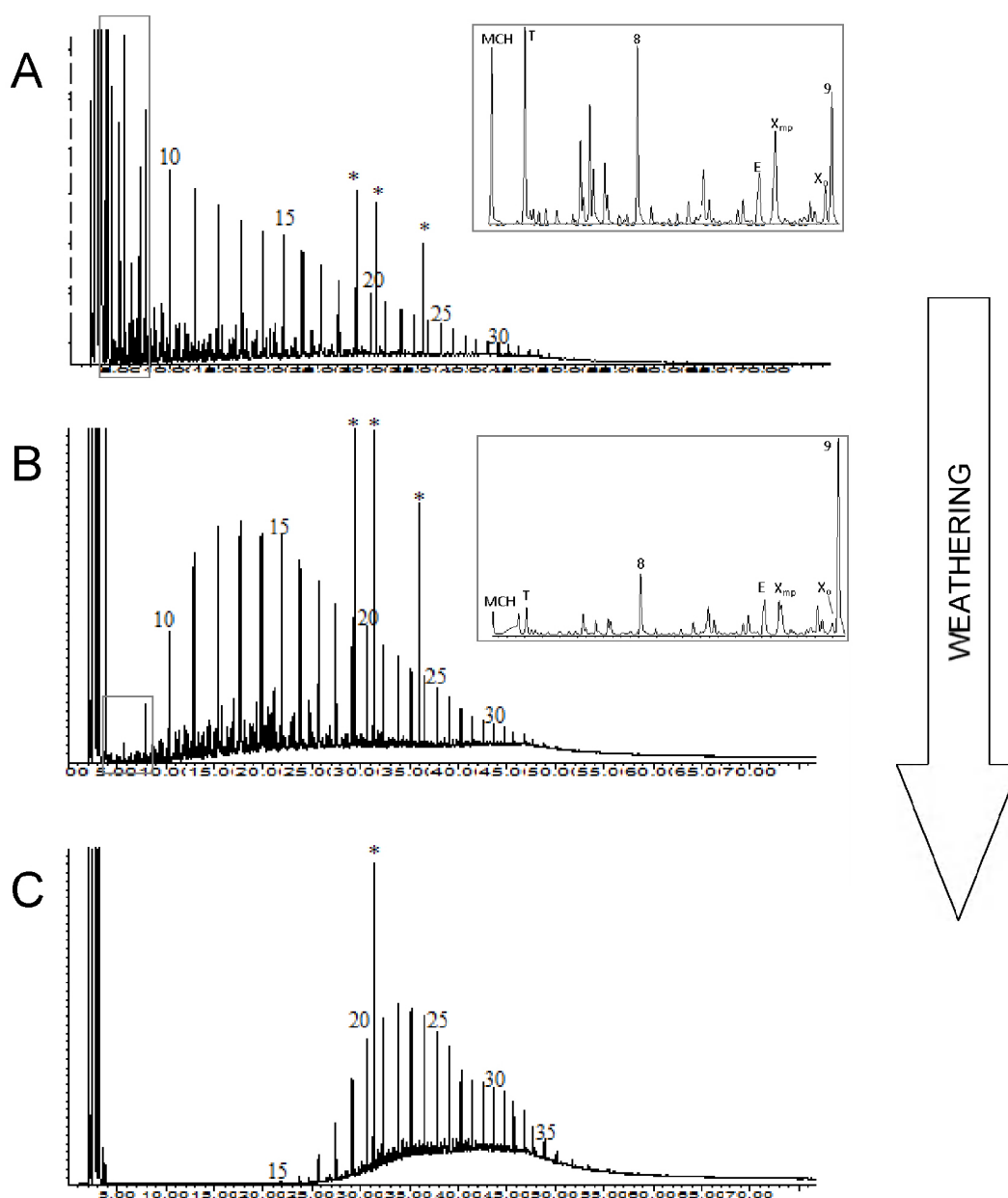
Figure 3: GC/FID chromatograms for (A) fresh Macondo oil (GU2988-A0521-O9805; 1005074-01), (B) a minimally weathered floating oil (JF3-2km-onet-20100616-surf-N143; 1007189-14D), and (C) a severely weathered floating oil (GU-10-02005-T-003; 1007190-13). Insets in (A) and (B) show volatiles between methylcyclohexane (MCH) and n-C_9 (9) in (A) and (B); * - internal standard; #: n-alkane carbon number, T-toluene, E-ethylbenzene, X_{mp} – m/p-xylenes, X_o – o-xylene. Note some toluene, ethylbenzene and xylenes are still present in (B). Inset in (C) shows %depletion of n-alkanes, pristane, and phytane per Eq. 2. Sample shown in (B) was collected immediately upon surfacing and represents the freshest floating Macondo oil studied.

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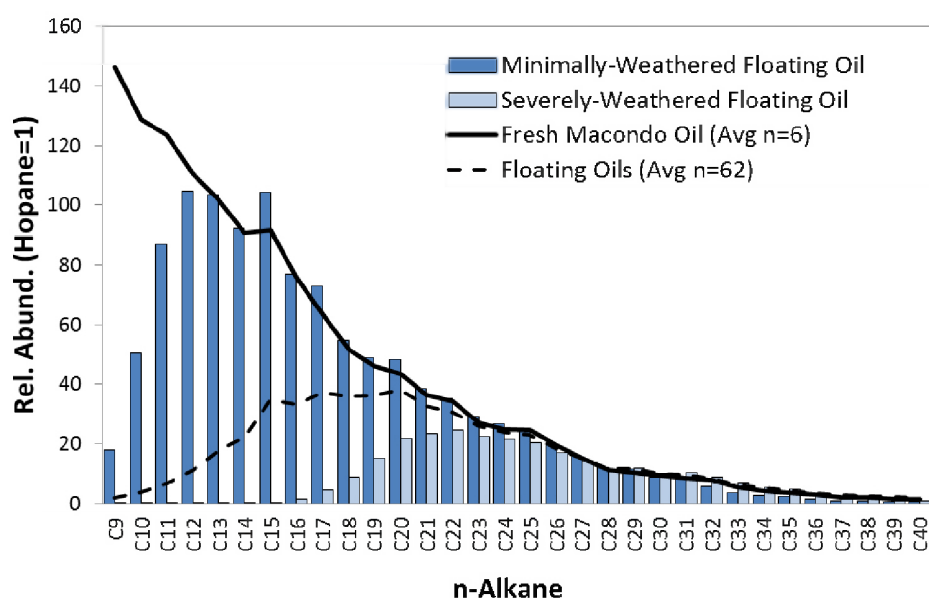
Figure 4: Hopane-normalized histograms for minimally and severely weathered floating oils versus fresh Macondo oil and the average of all floating oils studied. Minimally and severely weathered oils are same as shown in Fig. 3B and 3C. Fresh oil data from Stout (2015b). The minimally weathered floating oil (JF3-2km-onet-20100616-surf-N143) was collected immediately upon surfacing and represents the freshest floating Macondo oil studied.

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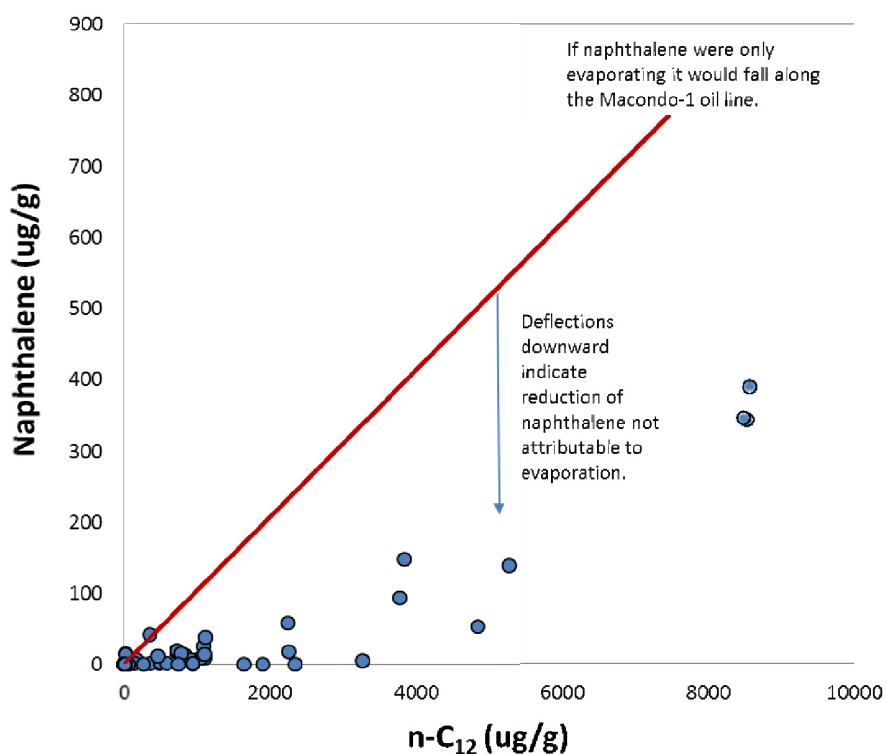
Figure 5: Cross-plot of n-dodecane versus naphthalene concentrations (ug/g oil) in floating Macondo oil demonstrating reduced naphthalene concentrations relative to n-dodecane indicating naphthalene was likely dissolved into seawater, not only evaporated. Dissolution of naphthalene (and other soluble hydrocarbons) likely occurred both at the sea surface and during vertical transport from the wellhead.
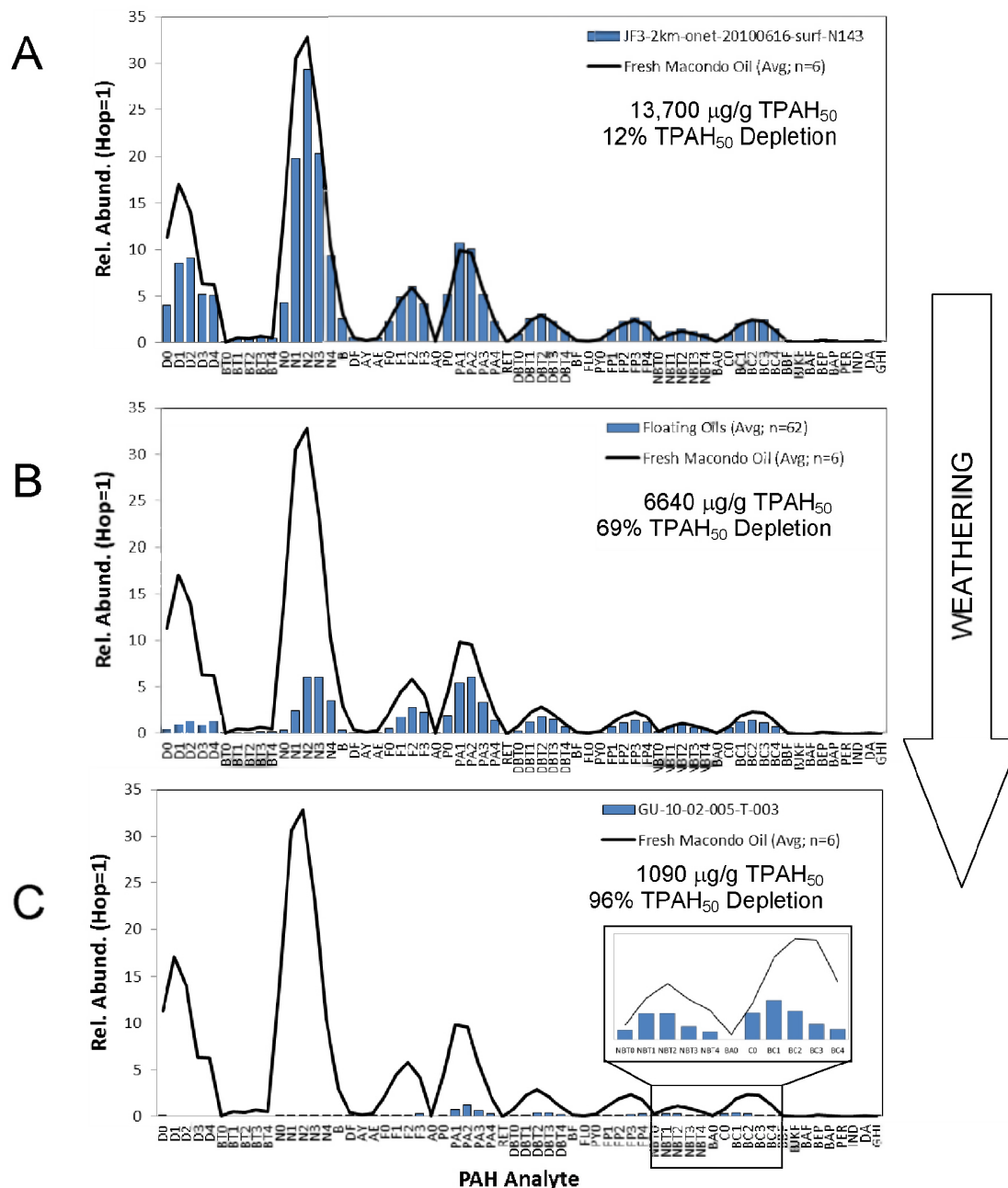
Figure 6: Representative hopane-normalized PAH and related compound histograms for variously weathered floating Macondo oils from spring and summer 2010. (A) a minimally weathered floating oil, (B) average of all floating oils, and (C) a severely weathered floating oil. %TPAH$_{50}$ (N0-GHI, excluding RET and PER) depletion calculated as per *Eq.* (2). Compound abbreviations from Table 3. The minimally weathered floating oil (A) was collected immediately upon surfacing and represents the freshest floating Macondo oil studied.

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DWH-AR0038675
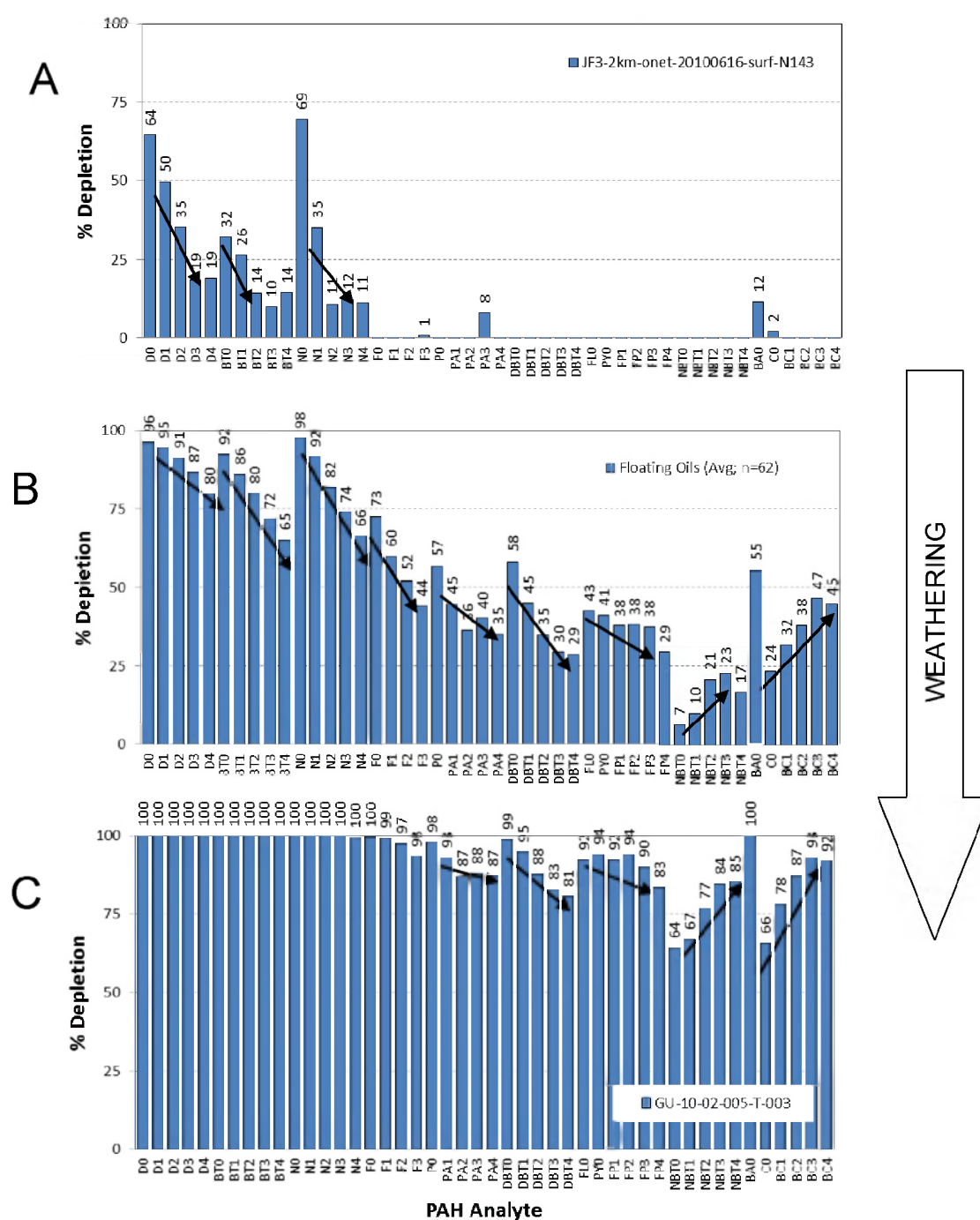
Figure 7: Percent depletions of individual PAHs for variously weathered floating Macondo oils from spring and summer 2010. (A) a minimally weathered floating oil, (B) average of all floating oils (n=62), and (C) a severely weathered floating oil. %Depletions relative to hopane calculated as per *Eq*. (2). Compound abbreviations from Table 3. The minimally weathered floating oil (A) was collected immediately upon surfacing and represents the freshest floating Macondo oil studied.
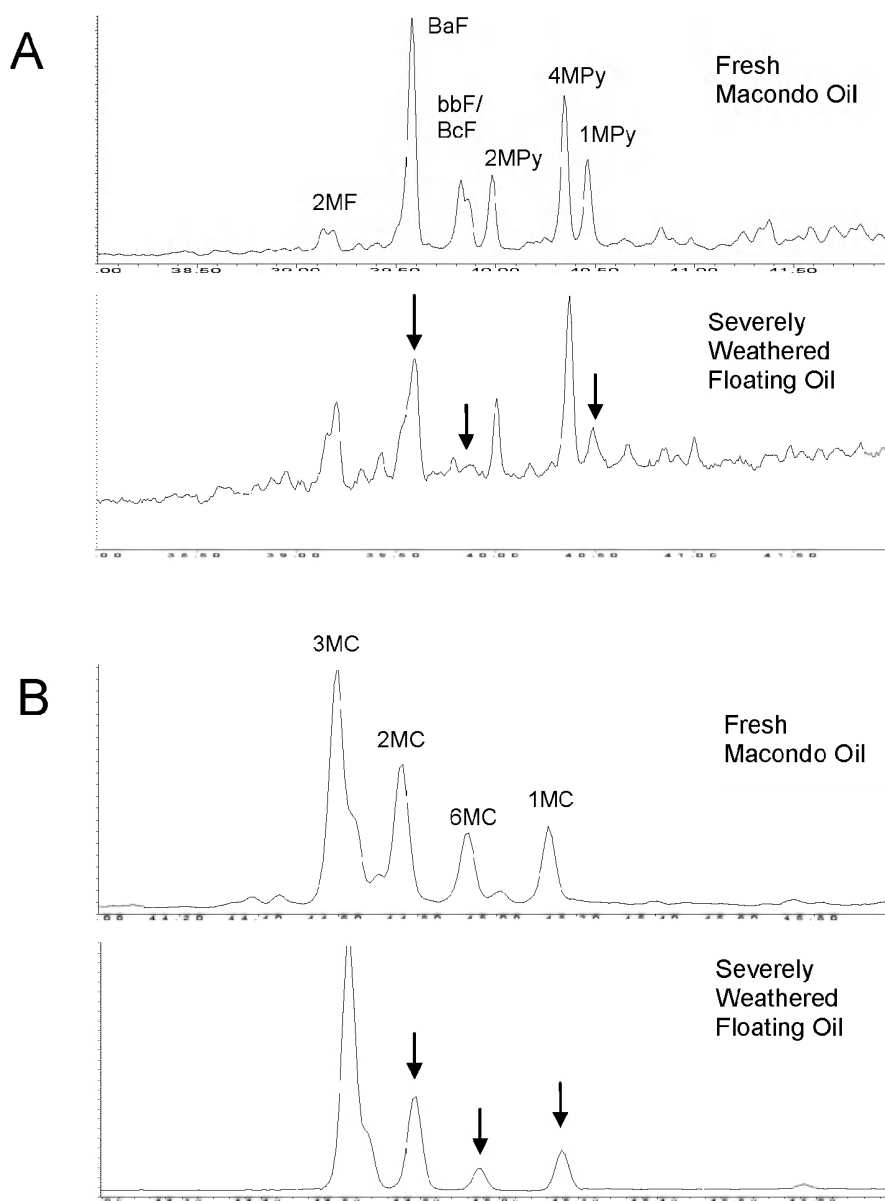
Figure 8: Partial EIPs showing PAH isomer changes in (A) methyl-fluoranthrenes/pyrenes and benzofluorenes (*m/z* 216) and (B) methyl-chrysenes (*m/z* 242) in fresh Macondo oil and a severely weathered floating Macondo oil (GU-10-02005-T-003). Isomer specific reductions (arrows) are attributed to photo-oxidation.

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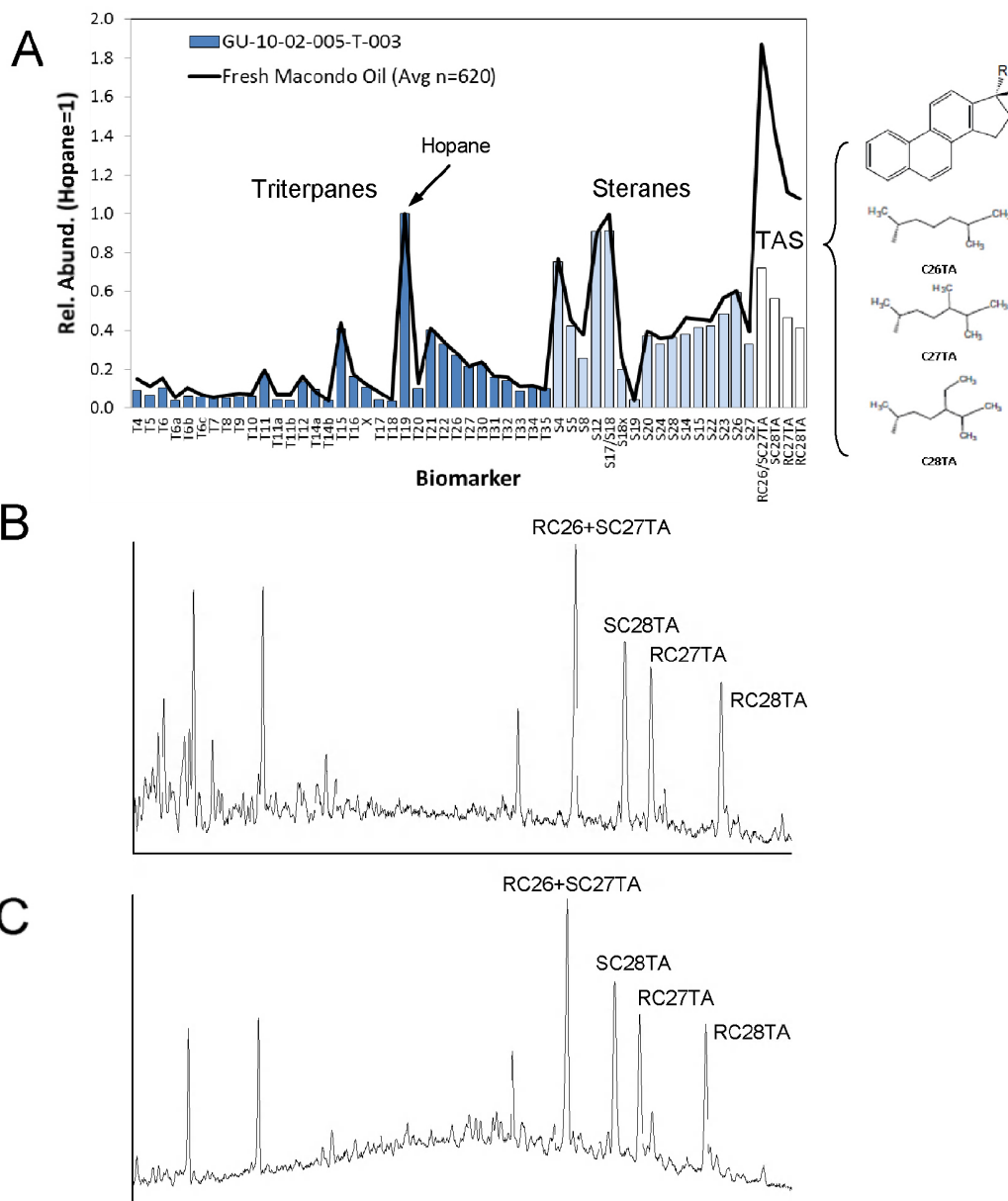
Figure 9: Triaromatic steroid (TAS) in fresh and severely weathered floating oil. (A) histograms showing hopane-normalized concentrations of triterpanes, steranes, and TAS. (B) partial *m/z* 231 EIP showing TAS congeners in fresh Macondo oil (GU2988-A0521-O9805). (C) partial *m/z* 231 EIP showing TAS congeners in a severely weathered floating Macondo oil (GU-10-02005-T-003). Compound abbreviations from NDRA AQAP (NOAA 2014).

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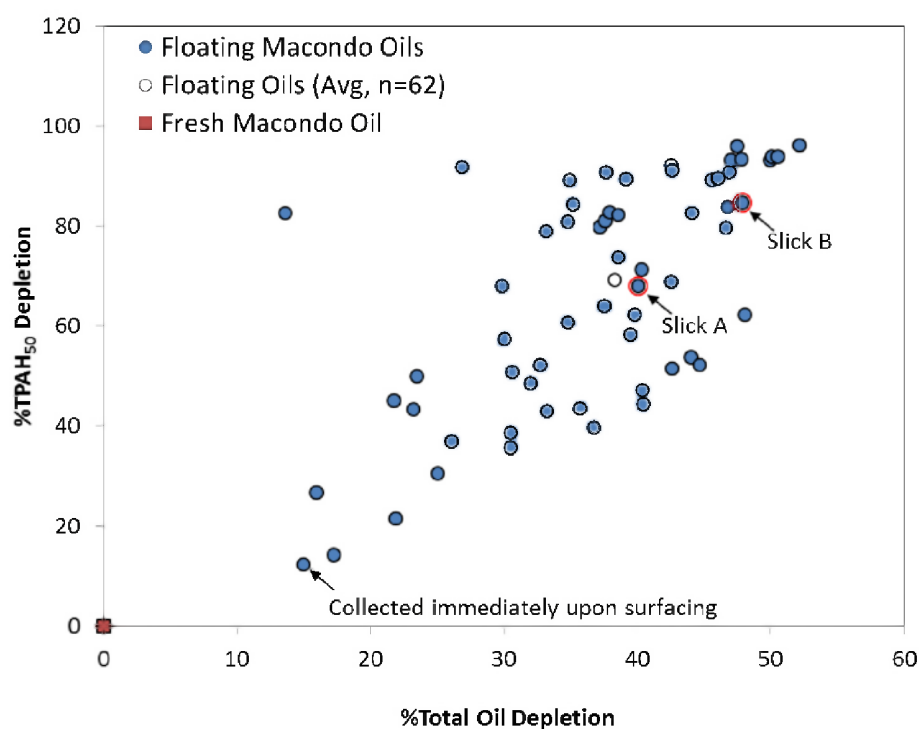
Figure 10: Cross-plot of %total oil depletion and %TPAH50 depletion for all 62 floating Macondo oils studied from spring and summer 2010. The large volume oils collected for toxicity testing – Slick A (CTC02404-02) and Slick B (GU2888-A0719-OE701 – are indicated. Slick B is more weathered than Slick A, the latter of which is very comparable to the average floating oils collected in the spring and summer of 2010. Note the oil collected immediately upon surfacing had already lost 15% total oil mass and 12% of TPAH50.
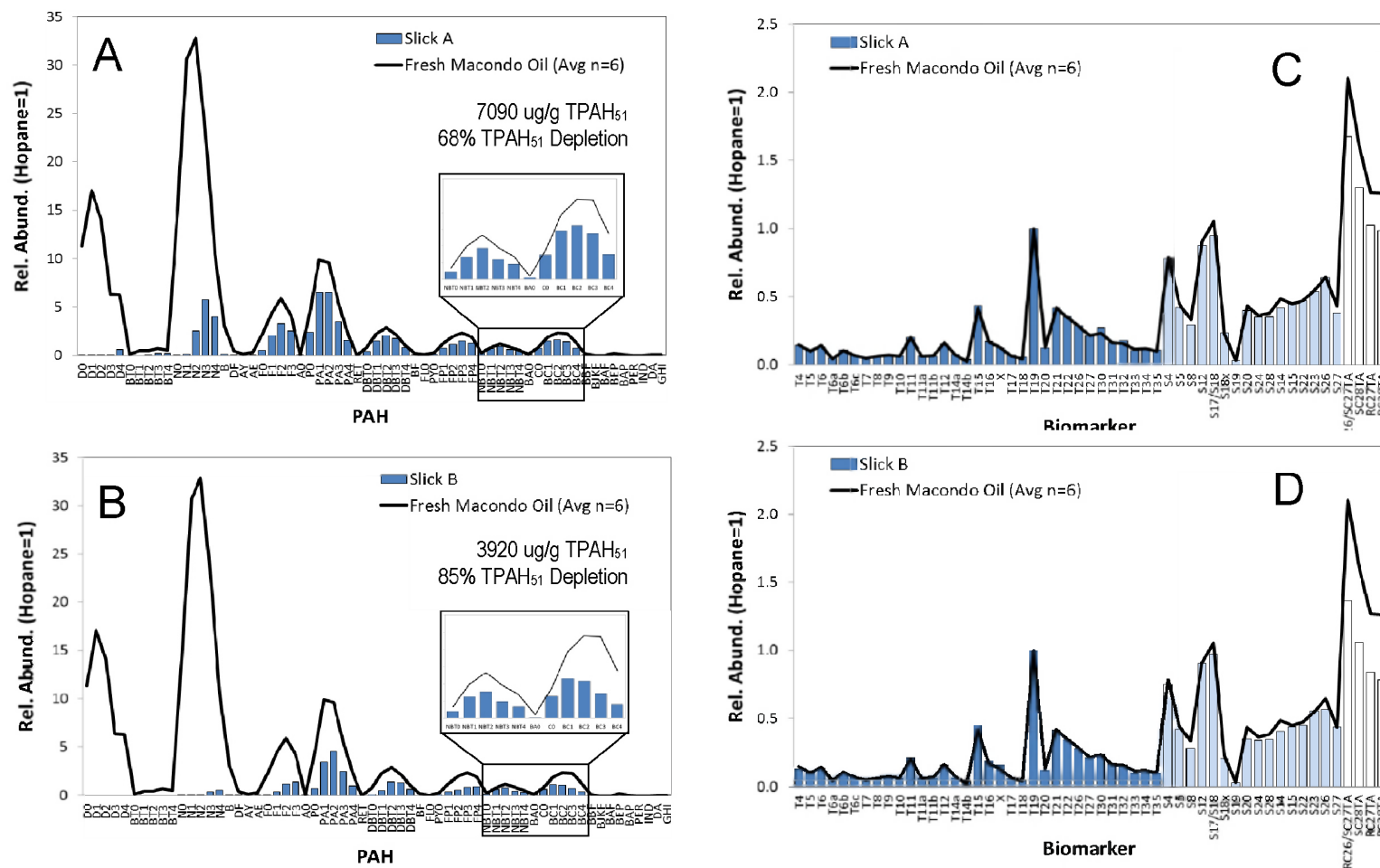
Figure 11: Hopane-normalized PAH and biomarker histograms for the Slick A and Slick B floating oils. (A) PAH in Slick A, (B) PAH in Slick B, (C) Biomarkers in Slick A, (D) Biomarkers in Slick B. %TPAH$_{50}$ (N0-GHI, excl RET and PER) depletion calculated as per Eq. (2). Slick A (CTC02404-02) and Slick B (GU2888-A0719-OE701). Effects of photo-oxidation on naphthobenzothiophenes (NBT0-4), benz(a)anthracenes/chrysenes (BaA-BC4), and TAS are more pronounced in Slick B. Compound abbreviations from Table 3.

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